BIOSORBED FERRO NANO-PARTICLES AS POTENTIAL AGENTS FOR THE REMOVAL OF SYNTHETIC FOOD DYES IN EFFLUENTS

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BY

RICHA SHARMA

UNDER THE SUPERVISION OF

Dr. SUDHIR KUMAR VERMA
(Assistant Professor)

Co-SUPERVISION OF

Dr. SOAMI P. SATSANGEE
(Professor)

PROF. SAHAB DASS
HEAD, DEPARTMENT OF CHEMISTRY

PROF. VIBHA RANI SATSANGE
DEAN, FACULTY OF SCIENCE

DAYALBAGH EDUCATIONAL INSTITUTE
(DEEMED TO BE UNIVERSITY)
DAYALBAGH, AGRA – 282005
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ORIGIN OF PROBLEM

An increase in human population and rapid growth of industrialization and urbanization has led to a great economic development and increased standard of living in developing countries, but at the same time we cannot deny the fact that this development is done at the cost of nature. Increased use of vehicles, fertilizers, chemicals, etc. has posed a great threat to our environment causing serious problems such as pollution; global warming etc. Out of all these issues, water pollution is a serious issue for people as water is the basic requirement for survival. Industrial wastes and domestic wastes is dumped or released into the water bodies (rivers, lakes, ponds, oceans etc.) leading to its contamination.

Recently, food, textile, printing and other related industries are facing problems of treatment and disposal of dye in waste water. Several countries discharge the effluent to surface water without any treatment because of technological and economical limitations. Out of all the pollutants, "Synthetic Food Dyes" are considered to be the major threat to ecosystem as they remain persistent due to their high stable nature. Tartrazine and Allura Red Dyes are widely used in food materials, confectionary products, drugs, cosmetics and textile industries.

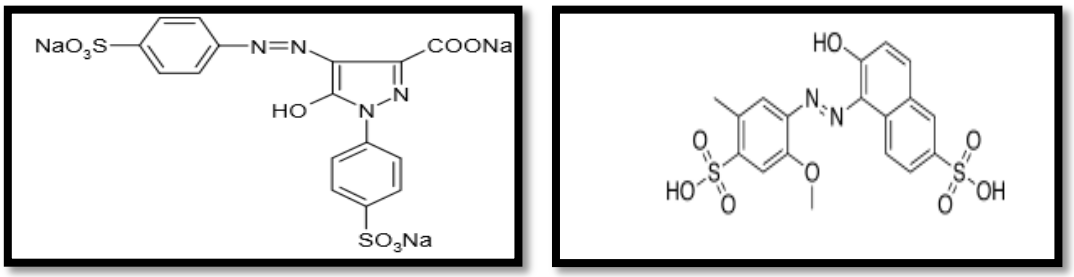
Thus, the present piece of work is aimed to remove Tartrazine and Allura Red Dyes from aqueous media by green routes using low cost nano-ferrofluid based bio-sorbents, developed from agricultural waste (Mustard Oil Cake, Water Hyacinth and Okra Seeds).

INTRODUCTION

An increase in human population and rapid growth of industries has triggered a high demand for dyes and pigments. Approximately 10,000 different dyes and pigments are used by industries and over 7×10^5 tons of dyes are annually produced worldwide (Mane *et al*., 2007). It is well known that most of dyes and pigments are produced from organic substances. Around 50% of all dye diversity is represented by azo dyes and due to their extensive applications and persistence they pose a clear environmental hazard (Chatterjee *et al*., 2010).The synthetic dyes are used in the food industries to improve the sensorial, technological and commercial aspects of the products, but due to their excess use they cause serious damages to the human health and environment (Pinto *et al*., 2014 and FDA 2013). Because of the high stability of the synthetic food dyes, the available conventional physico-chemical and biological removal methods may not be completely effective for their elimination (Attia *et al*., 2006).

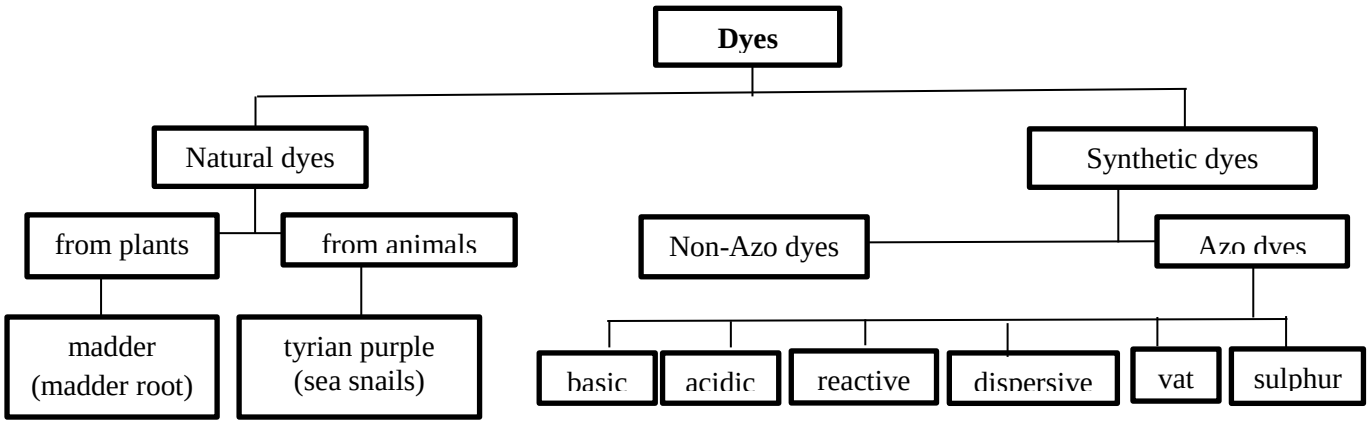
Several techniques have been used to treat colored effluents, for example oxidation (Wang *et al*., 2013), photocatalytic degradation (Saleh *et al*., 2012), coagulation (Morshedi *et al*., 2013) and adsorption (Wang *et al*., 2012). Among these available methods, adsorption is a popular technique because of its simplicity and high efficiency, as well as the availability of a wide range of adsorbents. It has proven itself an effective method for removal of various dyes from wastewaters. Another advantage of the adsorption process is that its sludge frees operation, and thorough removal of dyes even from dilute solutions. There is a growing interest in finding low cost, locally available and effective materials for the removal of dyes. Several non-conventional, low price adsorbents such as bentonite (Chatterjee *et al*., 2009), chitosan (Dotto *et al*., 2011) chitosan scaffold (Pinto *et al*., 2014), silica microspheres (Wang *et al*., 2012), activated carbon (Demirbas 2009) rice husk (Han *et al*., 2008) and fungi (Binupriya *et al*., 2008) have been used for the removal of azo dyes from aqueous solutions. The extensive use of chitosan as a dye adsorbent is due to its high hydro-philicity, presence of a large number of hydroxyl and amino groups with high activity as adsorption sites, non-toxicity, abundance in nature, biocompatibility, biodegradability, bioadhesivity, film-forming ability and most

of all, because of its exceptional chelating behavior (Piccin *et al*., 2011). In the powder form chitosan has disadvantages, such as, low values of specific surface area and void fraction (Kannusamy *et al*., 2013 and Pinto *et al*., 2014). Unfortunately, not all of these adsorbents are effective against anionic dyes due to their hydrophobic or anionic surfaces. Therefore, more efficient adsorbents are needed for the removal of synthetic food dyes from aqueous solutions. Tartrazine (TAR) and Allura Red (AR) are synthetic azo colorings (Figure 1a and 1b) used commercially in paper, foods, textiles, drugs and other products. Therefore, these soluble colored contaminants must be removed from aqueous solutions.

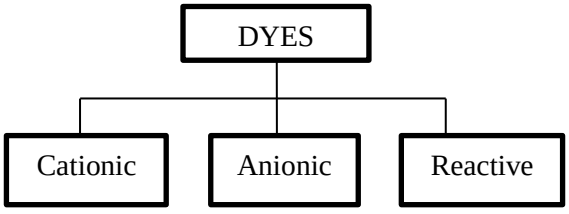


(a) (b)

Figure 1: The chemical structure of dyes: (a) Tartrazine; (b) Allura Red



DYES & THEIR TOXIC EFFECTS



Cationic dyes

Cationic dyes are also called basic dyes due to the presence of positive ions in the molecular structure. Basic dyes are water soluble and they are highly visible in water even at very low concentration. Basic dyes consist of monoazoic, diazoic and azine compounds (Lee *et al*., 2008). They are used to color wool, silk, nylon, mod-acrylic and polyester materials. Cationic functionality is found in various types of dyes such as cationic azo dyes, methane dyes, anthraquinone, di and tri-arylcarbenium, phthalocyanine dyes, polycarbocyclic and solvent dyes. Basic dyes are toxic and can cause allergic dermatitis, skin irritation, mutations, jaundice, quadriplegia and tissue necrosis in humans and even cancer (Eren *et al*., 2009 and Vadivelan *et al.*, 2005).

Anionic dyes

They have negative ions due to the excess presence of the OH^- ions in aqueous solution. Anionic dyes are water soluble and they include acid dyes, azo dyes, direct dyes and reactive dyes. Reactive dyes attach to their substrates by a chemical reaction (hydrolysis of the reactive groups in the water) that forms a covalent bond between the molecule of dye and that of the fiber (Demirbas 2009). Their removal is the most challenging task as they produce very bright colors in water and show acidic properties. The food dyes are generally anionic in nature.

Reactive dyes

They contain reactive groups such as vinyl sulphone, chlorotriazine, tri-chloropyrimidine, and di-fluoro-chloropyrimidine that covalently bonded with the fiber during the dyeing process. Moreover, azo dyes represent the largest class of reactive dyes used in the textile industry followed by anthraquinone and phthalocyanine classes (Jeng-Shiou *et al*., 2001). Azo dyes have the largest variety of dyes and under anaerobic conditions, the dye's linkage can be reduced to form aromatic amines which are colorless but can be toxic and carcinogenic (Yaneva *et al*., 2012). Some properties, applications and toxicities of various dyes have been tabulated as follows (Table 1).

Table 1: Properties, applications and toxicities of various dyes (Attia et al., 2006)

Dyes	Examples	Properties	Application	Toxicity
Cationic	Methylene blue, janus green, basic green 5, basic violet 10, rhodamine 6G.	Water-soluble, releasing colored cations in solution. Some dyes show biological activity.	Paper, polyacrylonitrile, modified nylons, modified polyesters, in medicine as antiseptics.	Carcinogenic (benign and malignant tumors).
Acidic	Acid red 183, acid orange 10, acid orange 12, acid orange 8, acid red 73, acid red 18, sunset yellow, acid green 27.	Water soluble, anionic.	Nylon, wool, silk, paper, leather, ink-jet printing.	Carcinogenic (benign and malignant tumors).
Disperse	Disperse orange 3, disperse red, disperse red 1, and disperse yellow1.	Water-insoluble, non-ionic; for hydrophobic aqueous dispersion.	Polyester, nylon, cellulose, cellulose acetate, acrylic fibers.	Allergenic (skin), carcinogenic.
Reactive	Reactive black 5, reactive green 19, reactive blue 4, reactive red 195, reactive blue 19,	Extremely high wash fastness due to covalent bond formation with fiber, brighter dyeing than direct dyes.	Cotton, wool, nylon, ink-jet printing of textiles.	Dermatitis, allergic conjunctivitis, rhinitis, occupational
Direct	Congo red, direct red 23, direct orange 39, direct blue 86.	Water soluble, anionic, improves wash fastness by chelating with metal salts.	Cotton, regenerated cellulose, paper, leather.	Bladder cancer
Vat	Vat blue 4, vat green 11, vat orange 15, vat orange 28, vat yellow 20.	Use soluble salts after reduction in an alkaline bath.	Cellulosic fibers.	Mutagenic to human and carcinogenic.
Synthetic Food Dyes	Tartrazine, Allura Red, Amaranth, Erythrosine, Sunset Yellow FCF, Brilliant Blue FCF.	They are brighter, more stable, cheaper, and available in a greater variety of colors.	Beverages, confectionery, processed foods, bakery products, dairy products, pet foods, colored sugar.	Teratogenic, carcinogenic, attention deficit hyperactivity disorder (ADHD), brain tumors.

LITRATURE REVIEW

PRESENT STATE OF KNOWLEDGE IN THE AREA OF RELEVANCE

Table 2: Some magnetic nanomaterial based adsorbents, targeted dyes and corresponding adsorption capacities

S. No	Dyes (Adsorbate)	Adsorbents	Maximum Adsorption Capacity (mg/g)	References
1.	Congo red	Magentic calcium ferrite nanoparticle ($CaFe_2O_4$)	40.933	An S. et al. (2015)
2.	Crystal violet	Magentic calcium ferrite nanoparticle ($CaFe_2O_4$)	0.836	An S. et al. (2015)
3.	Congo red + Crystal violet	Magentic calcium ferrite nanoparticle ($CaFe_2O_4$)	18.192	An S. et al. (2015)
4.	Methyl orange	Magnetic Fe/Ni nanoparticles doped bimodal mesoporous carbon	875.5	Liu Y. et al. (2015)
5.	Methyl orange	Chitosan/Al_2O_3/magnetite nanoparticles	417	Tanhaei B. et al. (2015)
6.	Reactive blue 19	Magnetic Fe_3O_4nanoparticles modified by pyrrole	112.36	Shanehsaz M.et al. (2015)
7.	Rhodamine B	Fe_3O_4/GO (graphene oxide) magnetic nanoparticles	238.5	Jiang G. et al. (2015)
8.	Violet 19	Polyaniline-Fe_2O_3 magnetic nanocomposite	0.99	Patil M. R. et al. (2015)
9.	Methyl blue (MB)	Fe_3O_4-GPTMS Lys	185	Zhang Y. R. et al. (2014)
10.	Methylene blue	Fe_3O_4-GPTMS Lys	141	Zhang Y. R. et al. (2014)
11.	Malachite green (MG)	Polyaniline-functionalized magnetic nanoparticles	240	Mahto T. K. et al, (2014)
12.	Reactive black 5	Graphite oxide/magnetic chitosan (GO–Chm)	391	Travlou N.A. et al. (2013)
13.	Methylene blue	Magnetic β-Cyclodextrin–chitosan	50.12	Fan L. et al. (2013)
14.	Rhodamine 6G	Nano-Fe_3O_4	55.8	Zhang X. et al. (2013)

Table 3: Agricultural based adsorbents, targeted dyes and corresponding adsorption capacities

S. No	Dyes (Adsorbate)	Bio-sorbent (Adsorbents)	Maximum Adsorption capacity (mg/g)	References
1.	Toluidine blue	Coffee waste	142.5	Lafi R et al. (2014)
2.	Methylene blue	Date stones	43.5	Ribas M.C. et al. (2014)
3.	Reactive (blue/red)	Palm shells	14-24.7	Auta M. et al. (2013)
4.	Congo red	Pine cone	19.18	Dawood S. et al. (2012)
5.	Methylene blue	Activated maize cob powder	70.29	Tan K. A. et al. (2012)
6.	Neutral red	Cottonseed hull	176.9	Zhou Qi et. al. (2011)
7.	Congo red	Papaya seeds	71	Poinern GEJ et al. (2011)
8.	Congo red	Sugar cane bagasse	38	Poinern GEJ et al. (2011)
9.	Malachite green	Neem bark	0.36	Ahmad R. et al. (2010)
10.	Malachite green	Mango bark	0.5	Ahmad R. et al. (2010)

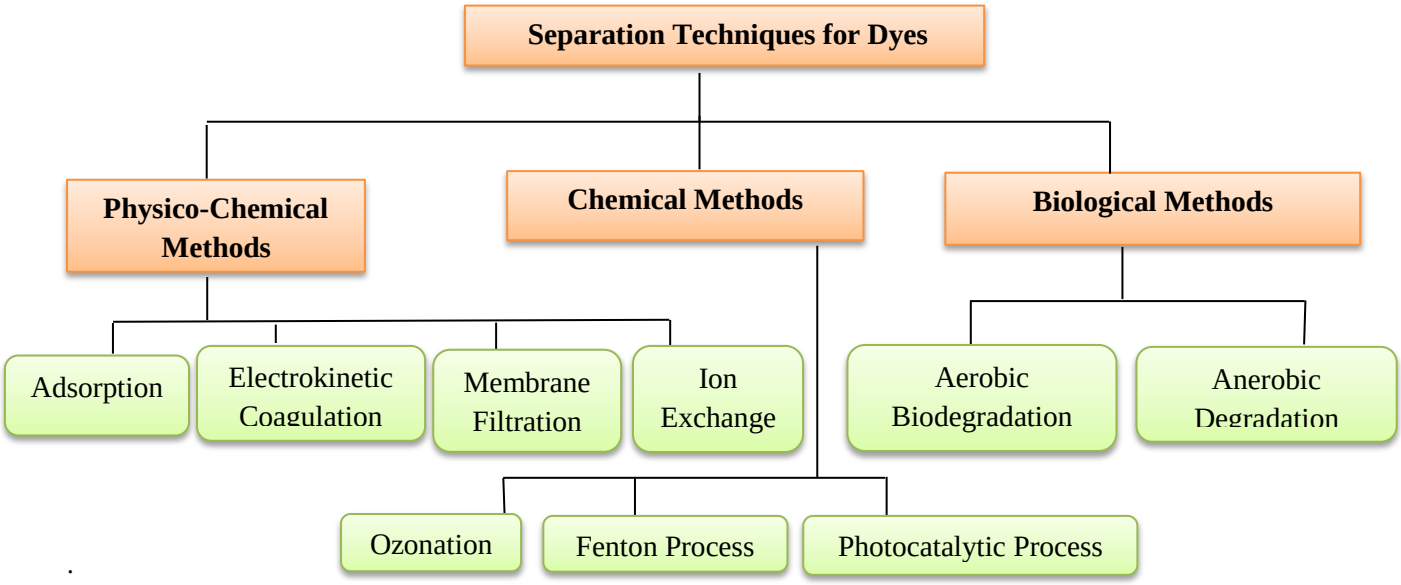
Table 4: Some Nanomaterial based adsorbents, targeted dyes and corresponding adsorption capacities

S. No	Dyes (Adsorbate)	Adsorbents	Maximum Adsorption capacity (mg/g)	References
1.	Methylene blue	Mesoporous silica nanoparticles	34.23	Qin P. et al. (2018)
2.	Rhodamine B	Mesoporous silica nanoparticles	23.26	Qin P. et al. (2018)
3.	Methyl violet	Mesoporous silica nanoparticles	20.36	Qin P. et al. (2018)
4.	Malachite green	Mesoporous silica nanoparticles	20.10	Qin P. et al. (2018)
5.	Basic fuchsin	Mesoporous silica nanoparticles	14.70	Qin P. et al. (2018)
6.	Methylene blue	CuO/MCM-41	87.8	Liang Z. et al. (2017)
7.	Methylene blue	CCMSN	43.03	Zhou Li. Y. et al. (2015)
8.	Methylene blue	S16C-30	561	Tsai C. H. et al. (2015)
9.	Remazol red 3BS	Hydrotalcite-based Nanocompounds	134.4	Asouhidou D. D. et al. (2012)
10.	Methylene blue	Exfoliated grapheme oxide	17.3	Ramesha G. K. et al. (2011)
11.	Methylene blue	SBA-15 60	49.26	Huang C. H. et al. (2011)
12.	Janus green B	SBA-15 60	66.44	Huang C. H. et al. (2011)
13.	Reactive blue 19	Nano-MgO	166.7	Moussavi G. et al. (2009)
14.	Methylene blue	Carbon nanotube	46.2	Eom D. et al. (2009)
15.	Remazol red 3BS	Synthetic mesoporous carbons	500–580	Asouhidou D. D. et al. (2009)

Table 5: Some Polymer Based Adsorbents, targeted dyes and corresponding adsorption capacities

S. No	Dyes (Adsorbate)	Adsorbents	Maximum Adsorption capacity (mg/g)	References
1.	Methylene blue	Functional polymer particles	1603	Chen D. et al. (2016)
2.	Azo dyes	Synthetic polymer	1428.6	Panic V. V. et al. (2013)
3.	Direct red 80	Poly (amidoamine-co-acrylic acid) copolymer	3448	Min M. et al. (2012)
4.	Sunset yellow FCF	Poly (ether sulfones) / poly (ethyleneimine) (PES/PEI) nano fibrous membrane	1000	Min M. et al. (2012)
5.	Janus green B	Poly (acrylamide-co-sodium 4-styrenesulfonate)	67%	Uzum O. B. et al. (2012)
6.	Orange II	Poly (N-isopropyl acrylamide-co-acrylic acid) microgel assemblies	73%	Parasuraman D. et al. (2012)
7.	Reactive red	Poly Pyrrole saw dust composite	204.08	Palanisamy P. N. et al. (2012)
8.	Congo red	Porous poly (vinyl alcohol) gels	35%	Sandeman S. R. et al. (2011)

CONVENTIONAL TECHNIQUES USED FOR DYES REMOVAL



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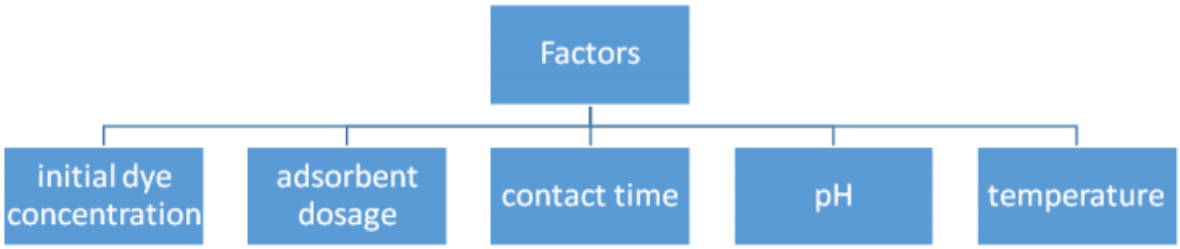
ADSORPTION

Adsorption process is a very effective separation technique and it is considered to be superior compared to other available techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances (Latif-Abd *et al*., 2010). Adsorption technique is a good way to treat highly colored effluents, because of its advantages compared to the available conventional methods, mainly from the environmental and economic point of views (Dotto *et al*., 2011). The efficiency of adsorption process depends on the physical and chemical properties of the adsorbent and adsorbate. The selection of the adsorbents is based on the adsorption capacity, surface area, availability and total cost.

FACTORS AFFECTING ADSORPTION



Effect of initial dye concentration

The initial dye concentration of an effluent is important since a given mass of sorbent material can only adsorb a fixed amount of dye. The effect of the initial of dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface (Artioli *et al*., 2008).

Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption process can be carried out by preparing adsorbent-adsorbate solution with different amount of adsorbents added to in a particular initial dye concentration and shaken together until equilibrium time (Ansari *et al*., 2011).

Effect of contact time

The effect of contact time on adsorption of dye can be carried out by preparing adsorbent-adsorbate solution with fixed adsorbent dose and initial dye concentration for different time intervals and shaken until equilibrium (Ansari *et al*., 2011).

Effect of pH

pH is a measure of acidity or basicity of an aqueous solution. The pH factor is very important in the adsorption process especially for dye adsorption. At high pH solution, the positive charge at the solution interface decreases and the adsorbent surface appears negatively as a result, the cationic dye adsorption increases and anionic dye adsorption shows a decrease (Wongwailikhit *et al*., 2011).

Effect of temperature

A study of the temperature dependence of adsorption reactions gives valuable knowledge about the enthalpy and entropy changes during adsorption. Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process (Auta *et al*., 2013).

OBJECTIVES

- The proposed work is to examine the removal of Tartrazine and Allura Red food dyes from aqueous media by green routes using low cost nano-ferrofluid based bio-sorbents from Mustard Oil Cake (MOC), Water Hyacinth (WH) and Okra Seeds (OS) which is abundantly and cheaply available.
- The effect of operating parameters such as initial concentration of dyes, pH, particle size, contact time, temperature, and adsorbent dosage for the removal of dyes is proposed to be studies.
- Desorption studies will also be considered to make the proposed adsorbent (nano-ferrofluid based bio-sorbents) economical.

- Adsorption behavior is to be analyzed using Langmuir, Freundlich and Temkin isotherm models.
- The kinetic and the mechanism studies of adsorption will also be examined on the model of Weber-Morris and Boyd.

PLAN OF WORK: AT A GLANCE

❖ *Preparation of nano-ferrofluid based bio-sorbents from following agricultural byproducts-*

- Mustard Oil Cake (MOC)
- Water Hyacinth (WH)
- Okra Seeds (OS)

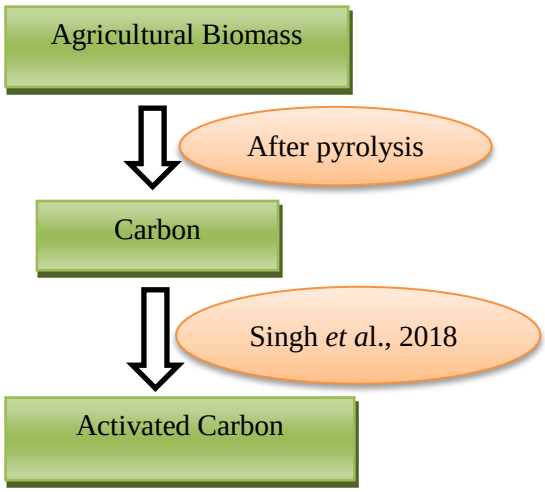
❖ *Characterization of the bio-sorbents-*

- ✓ Scanning Electron Microscopy (SEM)
- ✓ Fourier-Transform Infra-Red Spectroscopy (FTIR)
- ✓ X-Ray Diffraction Technique (XRD)
- ✓ Brunauer-Emmett-Teller (BET) Analysis
- ✓ Thermo Gravimetric Analysis (TGA)
- ✓ Atomic Force Microscopy (AFM)

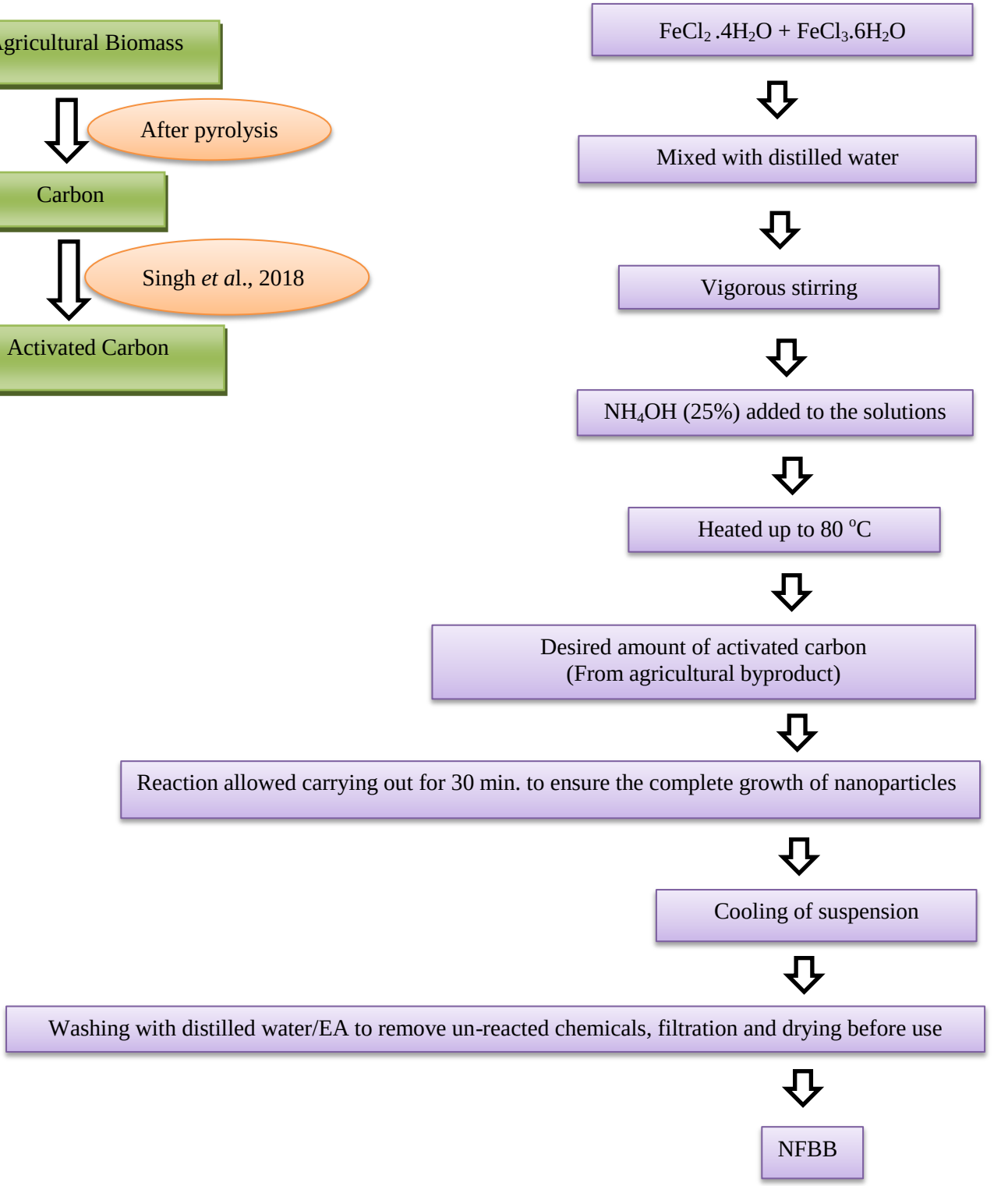
❖ *Study of following parameters on adsorption-*

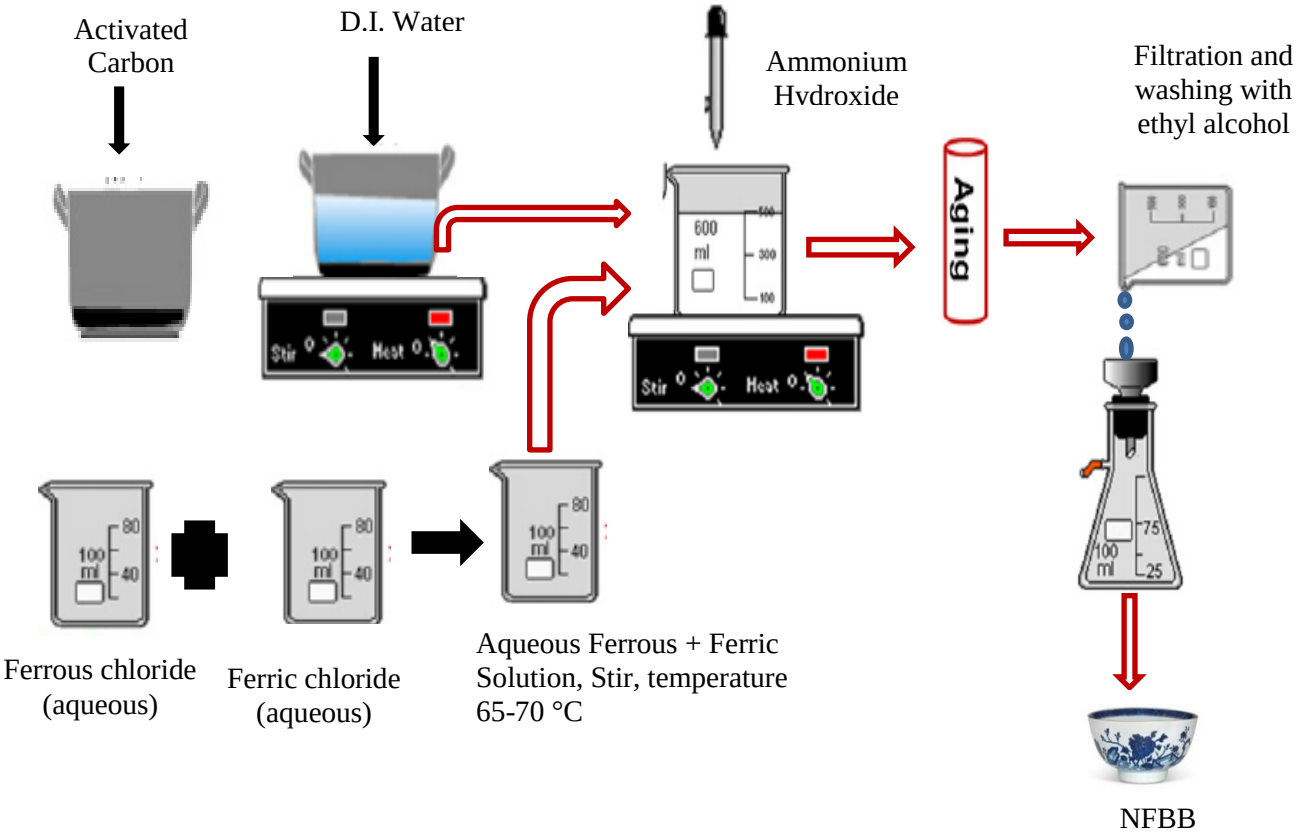
- ✓ Effect of pH
- ✓ Effect of contact time
- ✓ Effect of temperature
- ✓ Effect of adsorbent dosage
- ✓ Effect of particle size
- ✓ Effect of initial concentration of dye

Preparation of activated carbon



Preparation of nano-ferrofluid based bio-sorbent (NFBB)

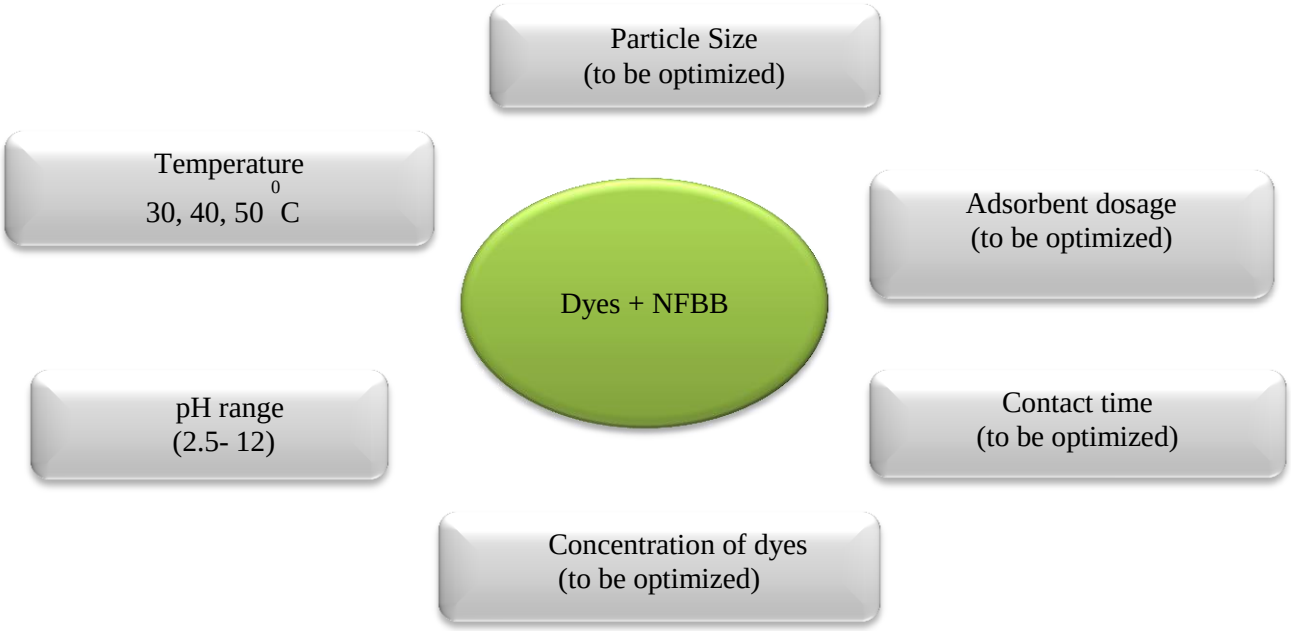

$FeCl_2.4H_2O + FeCl_3.6H_2O$
Mixed with distilled water
Vigorous stirring
NH_4OH (25%) added to the solutions
Heated up to 80 °C
Desired amount of activated carbon
(From agricultural byproduct)
Reaction allowed carrying out for 30 min. to ensure the complete growth of nanoparticles
Cooling of suspension
Washing with distilled water/EA to remove un-reacted chemicals, filtration and drying before use
NFBB



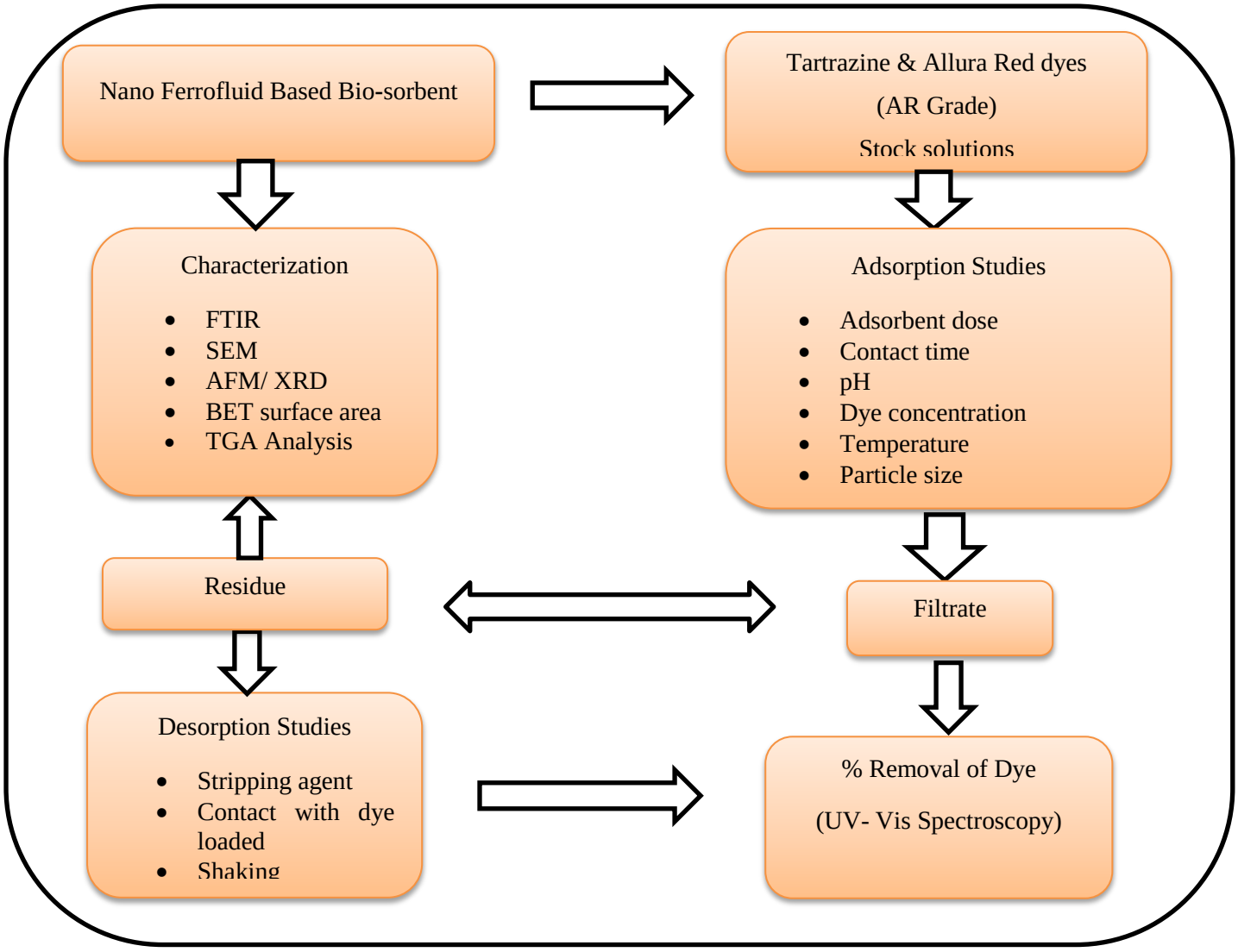
General scheme for the preparation of nano-ferrofluid based bio-sorbent (Mohana *et al*., 2011)

EXPERIMENTAL CONDITIONS FOR ADSORPTION

Adsorption efficacy at laboratory scale using standard practices would be carried out in batch experiments under various experimental conditions



EVALUATION OF SORPTION AND REGENERATION EFFICIENCY



Proposed preparation mechanism of the nano-ferrofluid based bio-sorbent

The proposed preparation mechanism of the nano-ferrofluid based bio-sorbent is based on co-precipitation technique because it is most adopted, simplest and most efficient technique for the synthesis of nano-ferrofluid based bio-sorbent. In this technique, the stoichiometric mixture of ferrous and ferric salts is aged in aqueous medium, and then the alkaline liquid-like aqueous ammonium hydroxide is added to form magnetic nanoparticle. The chemical formation of Fe_3O_4 is shown in the following equation (1).

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \longrightarrow Fe_3O_4 + 4H_2O \quad (1)$$

Magnetite (Fe_3O_4) is sensitive to oxidation, so it is not very stable and always transforms to maghemite (γ-Fe_2O_3) in the presence of oxygen, as shown in equation (2) (Shan *et al*., 2015).

$$Fe_3O_4 + 2H^+ \longrightarrow \gamma\text{-}Fe_2O_3 + Fe^{2+} + H_2O$$

Experiments revealed that the magnetism was caused by the ferromagnetic γ-Fe_2O_3 phase in the nanoparticles, which had a coating of ferric compound. This observation suggests that Fe^{2+} in the treatment solution underwent oxidation to Fe^{3+}, thereby inducing the magnetic transition. The transition was independent of the acid radical ions in the treatment solution, but the coating on the magnetic crystallites varied with changes in the acid radical ion.

The oxidation often occurs from the migration of cations through the lattice framework, and under such condition, the cationic vacancies are formed to maintain the charge. The cationic vacancies are the main differences between maghemite and magnetite. In ferrite, iron ions are distributed in the octahedral (Oh) and tetrahedral (Td) sites of the spinel structure $[Fe^{3+}]_{Td}$ $[Fe^{3+}\ Fe^{2+}]_{Oh}O_4$, but in maghemite, the cationic vacancies appear only in the octahedral sites (Laurent *et al*., 2008).

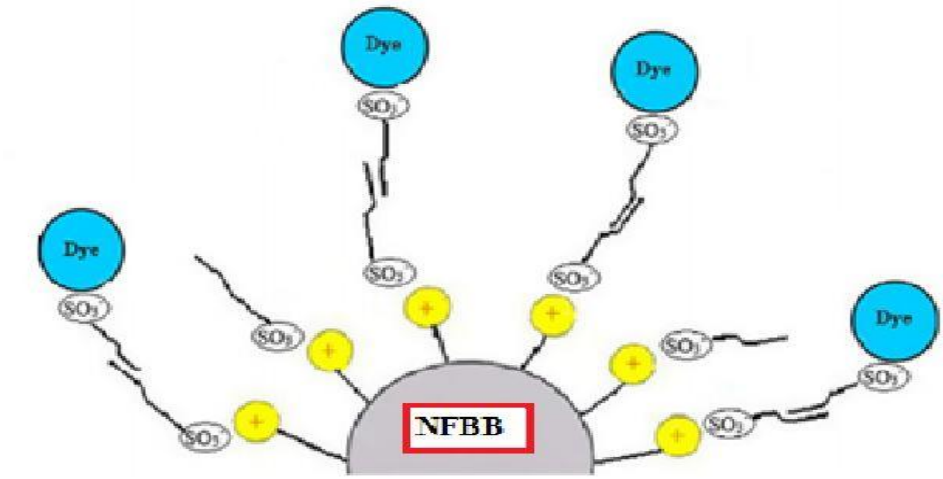
The overall reaction in the formation of nano-ferrofluid based bio-sorbent (NFBB) in the proposed research work.

$$FeCl_2.4H_2O + FeCl_3.6H_2O + NH_4OH \longrightarrow Fe_3O_4\ (s) + NH_4Cl + H_2O$$

Fe_3O_4 + AC (from agricultural byproduct) + H_2O ⟶ [NFBB] (s)

Proposed adsorption mechanism of the synthetic food dyes on NFBB

The surface of the nano-ferrofluid based bio-sorbent (NFBB) contained positive head group and sulphonated azo dyes have negative head group. The negative head group of the sulphonated azo dyes interact with the positive head group of the nano-ferrofluid based bio-sorbent (NFBB). In this condition, the anionic dye can be adsorbed on the surface of nano-ferrofluid based bio-sorbent (NFBB) due to high electrostatic force of attraction exists between the positively charged surface of nano-ferrofluid based bio-sorbent and negatively head group of the anionic dye (Keyhanian *et al.*, 2011).



Schematic diagram for the proposed adsorption mechanism

SIGNIFICANCE OF THE WORK

The proposed research work may be used for designed smart low cost adsorbent materials (nano-ferrofluid based bio-sorbent) with enhanced sorption potential, environmental stability and ability to chemical speciation. The research findings may be useful for designing low cost, domestic and eco-friendly method for remediation of toxic synthetic food dyes from water bodies from food industrial areas, particularly in Agra and Mathura region which has a number of food industries releasing food dyes in their effluent. The proposed method could be a potential challenge for conventional existing methods and lead to an innovative, economical and eco-friendly method for the remediation of synthetic food dyes.

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